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DOE Hydrogen Program

Non-Platinum Bimetallic Cathode Electrocatalysts

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Project ID: FC2

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Overview

Timeline

- Project start data: January, 2007
- Project end data: December, 2010
- Percentage complete: 30%

Budget

- Total project funding:
  - DOE: $5,434 K
  - Contractor share: $172 K
- Funding received in FY'07:
  - DOE: $1115 K
  - Contractor share: $35 K
- Funding for FY'08:
  - DOE: $1400 K
  - Contractor share: $42 K

Barriers

- **Barriers addressed**
  - A. Durability
  - B. Cost
  - C. Electrode performance

Partners

- California Institute of Technology (Caltech)
- University of Illinois at Chicago (UIC)
- University of Nevada at Las Vegas (UNLV)
- Oak Ridge National Laboratory (ORNL)
- Los Alamos National Laboratory (LANL)
- Lead Lab: Argonne

Objectives

- Develop a non-platinum cathode electrocatalyst for polymer electrolyte fuel cells to meet DOE targets that:
  - Promotes the direct four-electron oxygen reduction reaction (ORR) with high electrocatalytic activity
    (***0.44 A/mg$_{PGM}$; 720 μA/cm^2 @0.9 V$_{iR\text{-}free}$***)
    - *O_2 reduction reaction (ORR) in acidic media*
      - *Two-electron transfer*

        $O_2 + 2H^+ + 2e^- = H_2O_2$

      - *Four-electron transfer*

        $O_2 + 4H^+ + 4e^- = 2\ H_2O$
  - Is chemically compatible with the acidic electrolyte and resistant to dissolution (***<40% electrochemical area loss over 5000 h@≤80°C and 2000 h@>80°C***)
  - Is low cost (***$5/KW, 0.3 mg PGM/cm^2***)

- Objective in the past year:
  - Synthesize and evaluate the oxygen reduction activity, stability, and electronic structure of nano-particles of three palladium alloy systems (Pd-Cu, Pd-Ni, and Pd-Fe)

Approach

- Bimetallic systems (base metal-noble metal)
  - Surface segregation of minor noble metal component to form protective layer
  - Base metal component chosen to modify electronic properties of noble metal making it more “Pt-like”
  - Initial choice of bimetallic systems based on published surface segregation energies and d-band center shifts

    [A.V. Ruban, H.L. Skriver, J.K. Nørskov, Phys. Rev. B, 59 (1999)15990.; A. Ruban, B. Hammer, P. Stoltze, H.L. Skriver, and J.K. Nørskov, J. Mol. Catal. A 115 (1997) 421.]
  - Examples: Bimetallics of palladium, iridium, and rhodium

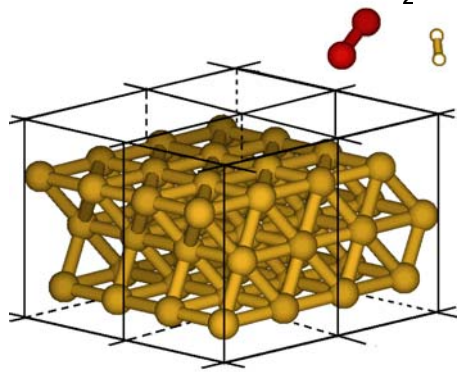
- How this project addresses the technical barriers
  - A. Durability: altering oxophilicity of catalyst to prevent oxidation-related degradation [J. Greeley and J.K. Nørskov, “Electrochemical dissolution of surface alloys in acids: Thermodynamic trends from first-principles calculations”, Electrochim. Acta 52 (2007) 5829-5836.]
  - B. Cost: lowering PGM loading by replacing PGM in electrocatalyst particle core with base metal
  - C. Electrode performance: modifying surface electronic properties to enhance ORR activity

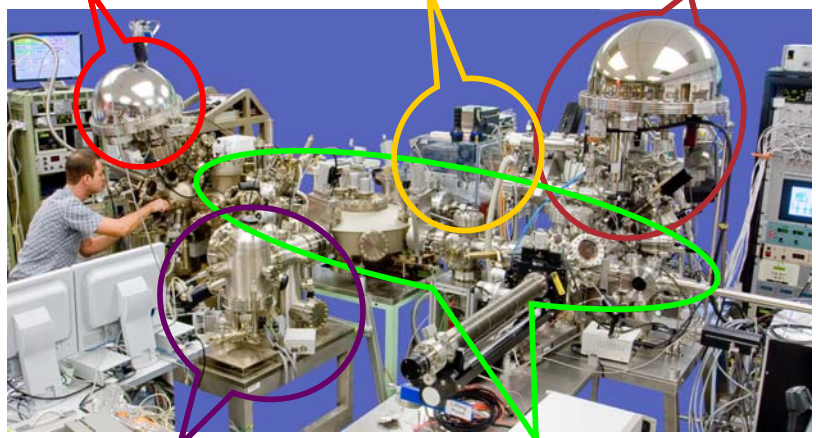
Project tasks

- Computational studies (Caltech)
  - Guide choice of systems and compositions
  - Quantum mechanical and large scale molecular dynamics for reaction pathways, kinetics, and preferred catalyst structures
- Model systems: bulk electrode fabrication and characterization (UNLV, Argonne)
  - Guide choice of systems and compositions
- Nano-particle synthesis on high-surface-area carbon support (Argonne, UIC)
- Nano-particle characterization (Argonne, ORNL, UNLV, UIC)
  - ORR activity, stability, composition, electronic structure, and morphology
- Membrane-electrode assembly fabrication and testing (LANL, ORNL)
  - Performance and durability using accelerated test protocol

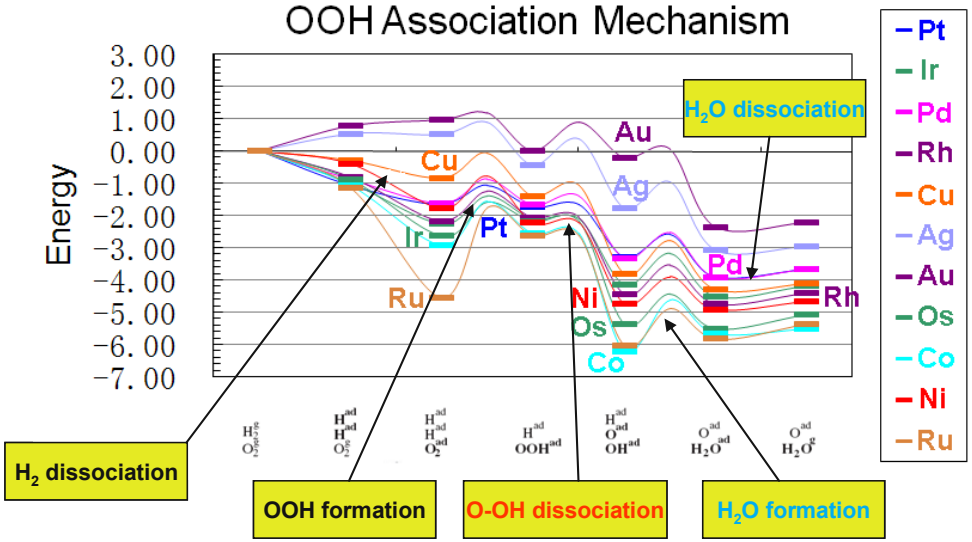
$2H_2 + O_2 \rightarrow 2H_2O$

ORR intermediates: H, O, OH, O_2,OOH, H_2O





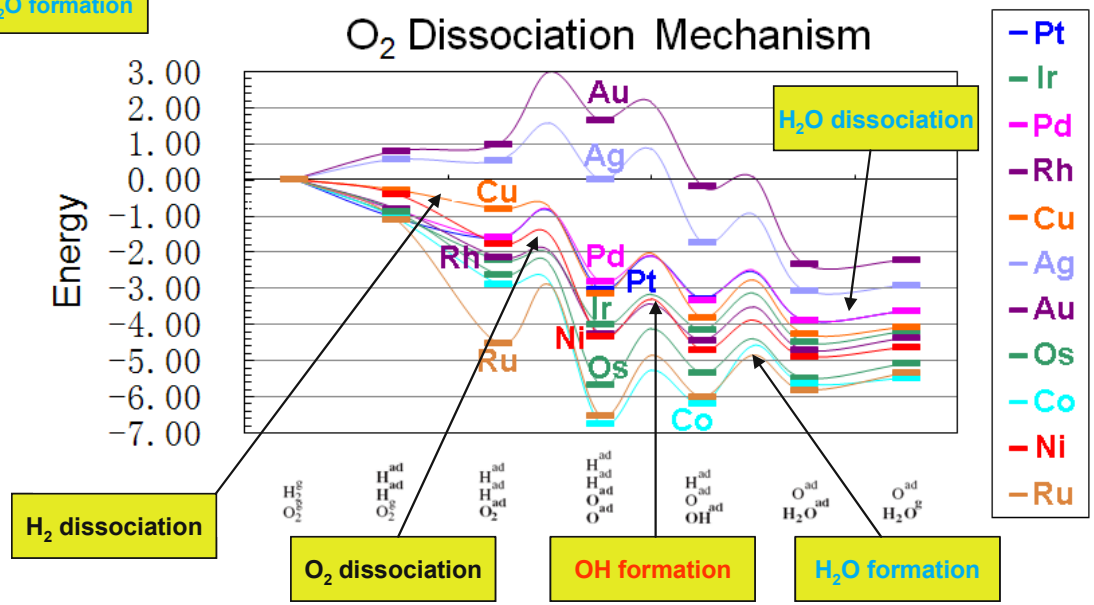
Energetics and reaction barriers for the two ORR mechanisms by periodic quantum mechanical slab calculations



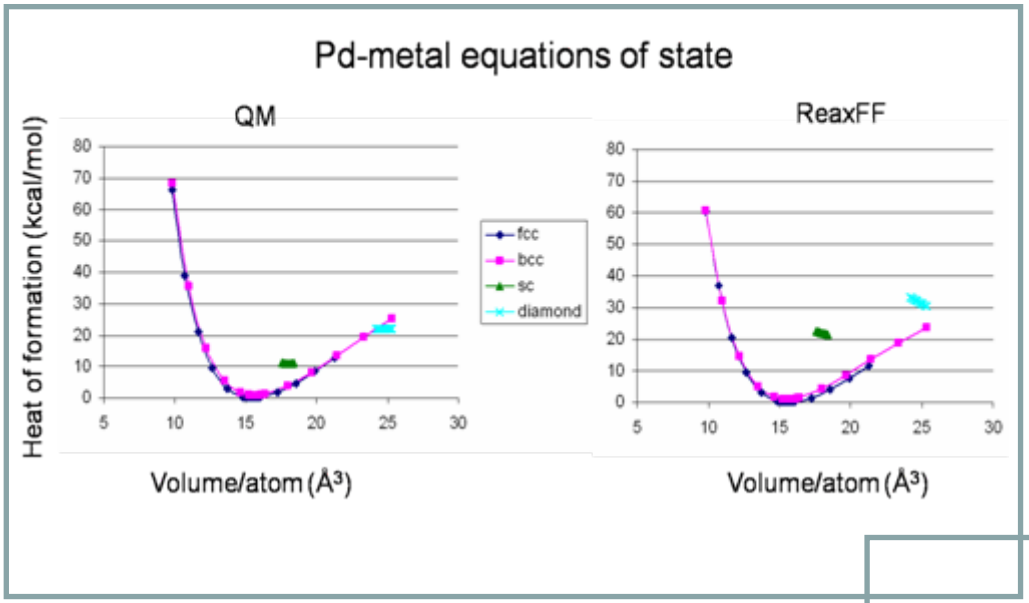
(111) surface, four atoms per layer, three layer slab

- Associative mechanism through OOH formation:
  - Rate-determining step on Pt, Pd, and Cu is H_2O formation
  - Barriers: Cu > Pd > Pt

- Dissociative mechanism through OH formation:
  - Rate-determining step:
    - *Pd: H_2O formation*
    - *Pt and Cu: OH formation*
  - Barriers: Cu >> Pt > Pd

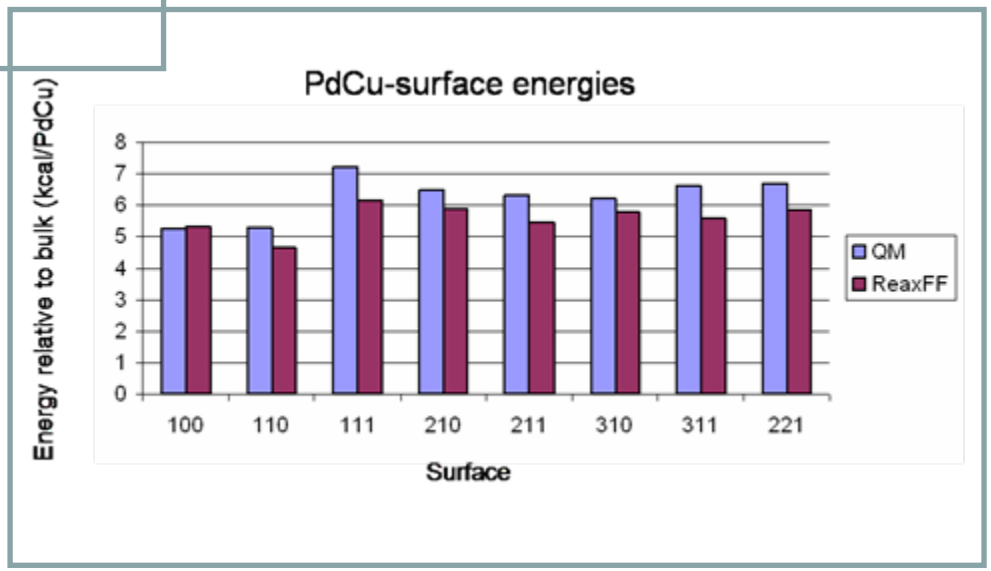


Large scale molecular dynamics (ReaxFF) potentials are being developed for PdCu alloys



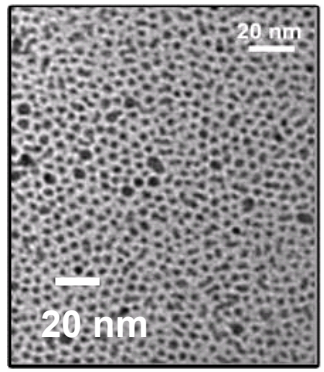
- ReaxFF gives a good description of Pd and PdCu-bulk structures

- ReaxFF reproduces Pd and PdCu surface energies as determined by quantum mechanical calculations

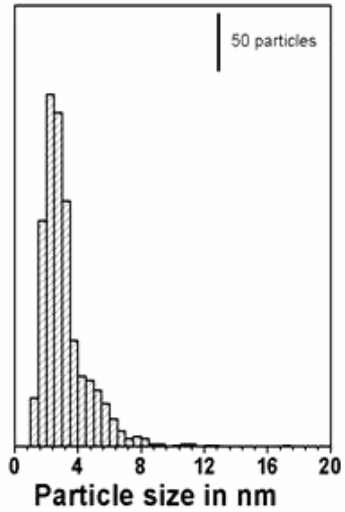


Synthesis of nano-particle bimetallic carbon-supported electrocatalysts

- Goals
  - Achieve noble metal-base metal bimetallic core with noble metal skin
  - Minimize particle size, maximize surface area/gram PGM
  - Achieve uniform and controllable particle size and composition



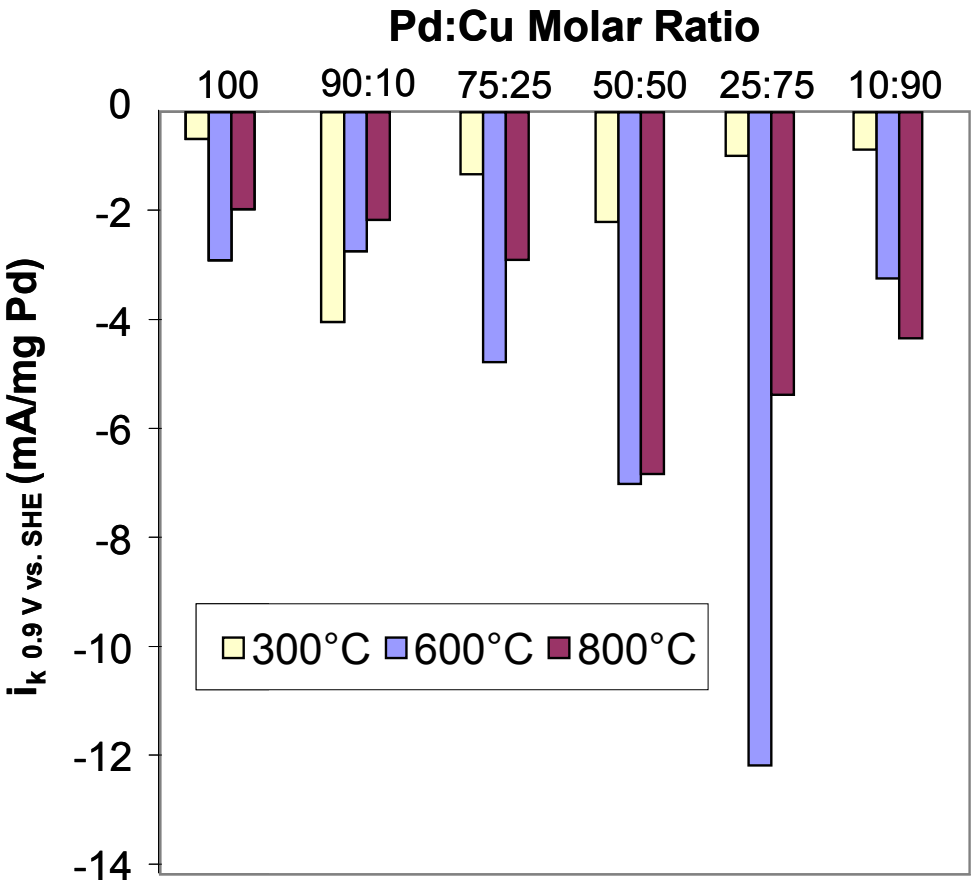
- Techniques
  - Impregnation (Argonne)
    - *Quick screening of noble metal-base metal ratio*
    - *High temperatures needed to promote alloy formation*
    - *Relatively large poly-disperse particles*
  - Single-Phase colloidal (Argonne)
    - *Small, relatively mono-disperse particles*
      - particle growth limited by presence of organic capping molecules
    - *Alloys formed at low temperatures*
  - Strong electrostatic adsorption (UIC)
    - *Small particles with controllable particle size*
    - *Core-shell particles can be formed by tuning solution pH*



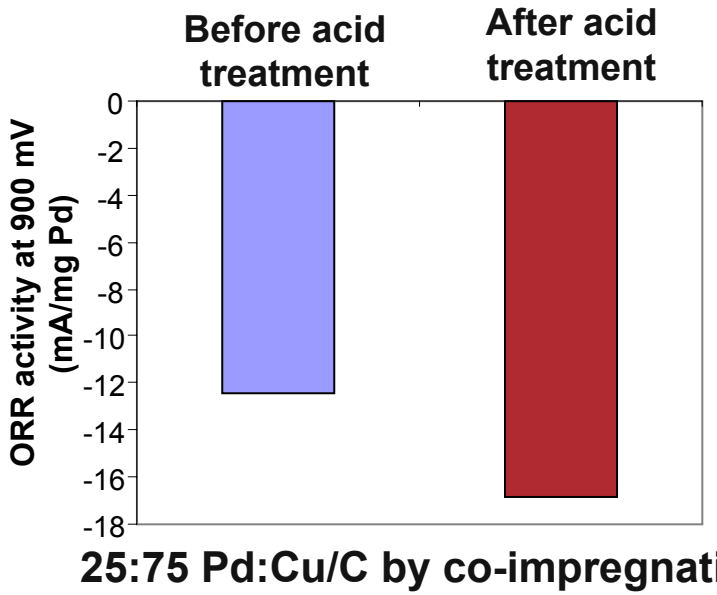
Summary of systems studied this year

Technique	Impregnation				Colloidal		Strong Electrostatic Adsorption	
System	**Pd**	**Pd-Cu**	**Pd-Ni**	**Pd-Fe**	**Pd**	**Pd-Cu**	**Pd**	**Pd-Co**
Composition Pd:BM Molar Ratio	100	90:10 75:25 50:50 40:60 33:67 25:75 10:90	90:10 75:25 50:50 25:75 10:90	75:25 55:45 50:50 30:70 10:90	100	50:50 25:75	100	8:92 14:86 22:78 36:64 53:47
Carbon support	VC	VC	VC	VC	VC	VC	VC BP 2000 Ox. VC Ox. BP	VC
Pd Precursor	Nitrate	Nitrate	Nitrate	Nitrate	Acetate	Acetate	Chloride	Amine nitrate
BM Precursor		Nitrate	Nitrate	Nitrate		Acetate	Amine nitrate	Nitrate
Heat-treatment Temp. (°C)	800	300, 400 450, 500 550, 600 800	400 500 600 700	450, 500 550, 620	300, 500 550	300, 400, 500, 550	200-800	200, 450 500
Heat-treatment atm. (H_2 %)	3.7	3.7 100	3.7 100	3.7 100	3.7 100	3.7 100	100	100

Summary of ORR activity of Pd-Cu prepared by co-impregnation



- Pd:Cu ratio of 25:75 shows the highest ORR activity per mg Pd
- Acid treatment enhances ORR activity of co-impregnated 25:75 Pd:Cu



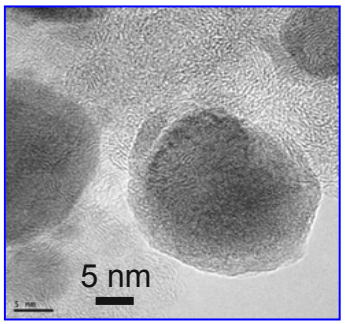
- Detailed description of these results are shown in last year's annual review poster (2007 AMR, FCP-28)

Characterization of Pd-Cu catalyst with highest area-specific ORR: acid-treated 25:75(Pd:Cu)-600°C

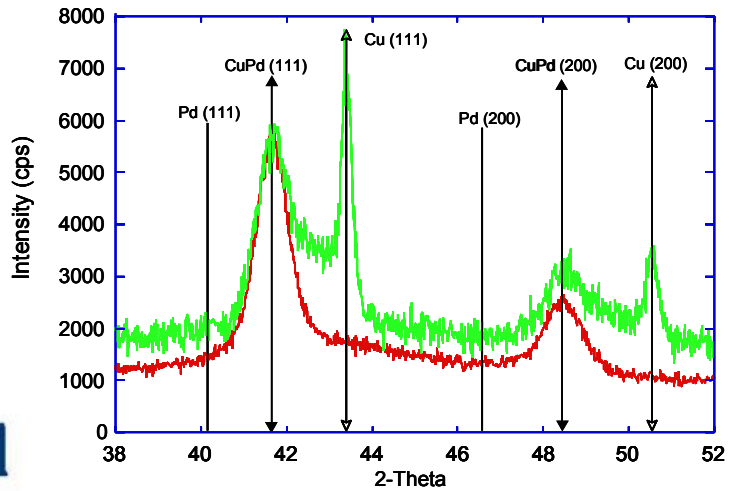
- ORR Pd mass activity increased by 30% with acid treatment; free copper removed
- ***Estimated*** specific ORR activity: 129 μA/cm² @ 900 mV
- 3.7 wt% Pd and 1.0 wt% Cu (68 mol% Pd:32 mol% Cu) (ICP-AES)
- Mean particle size of 21.5 ± 7 nm (TEM)
- $Pd_{49}Cu_{51}$ fcc particle core with Pd-rich surface (XRD; XPS)
- Thin, oxidized Pd-rich layer on $Pd_{49}Cu_{51}$ alloy core (XAFS)

TEM and XRD @ ORNL

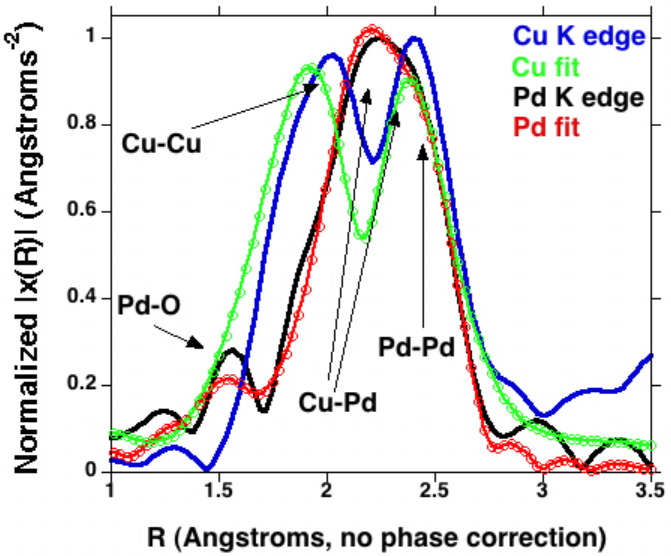
Before acid treatment



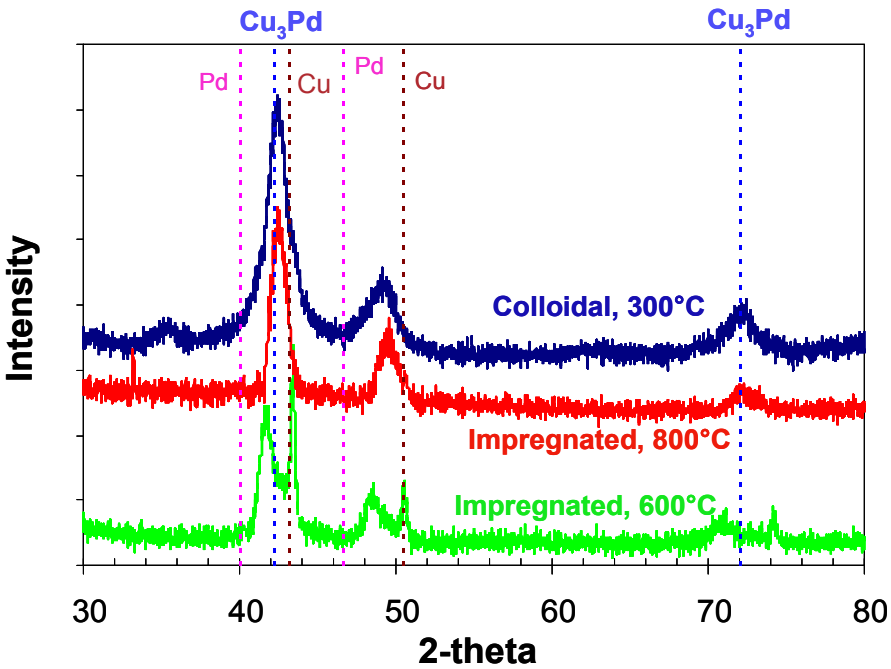
XRD Before and After acid treatment

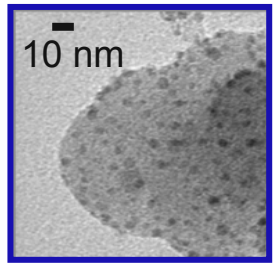


X-ray Absorption (XAFS)@ANL

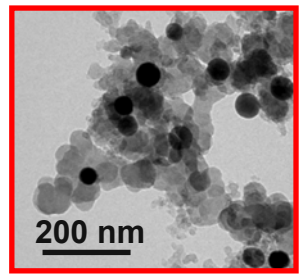


The colloidal technique was used to form Pd-Cu alloys of desired composition and to reduce particle size





Colloidal
300°C

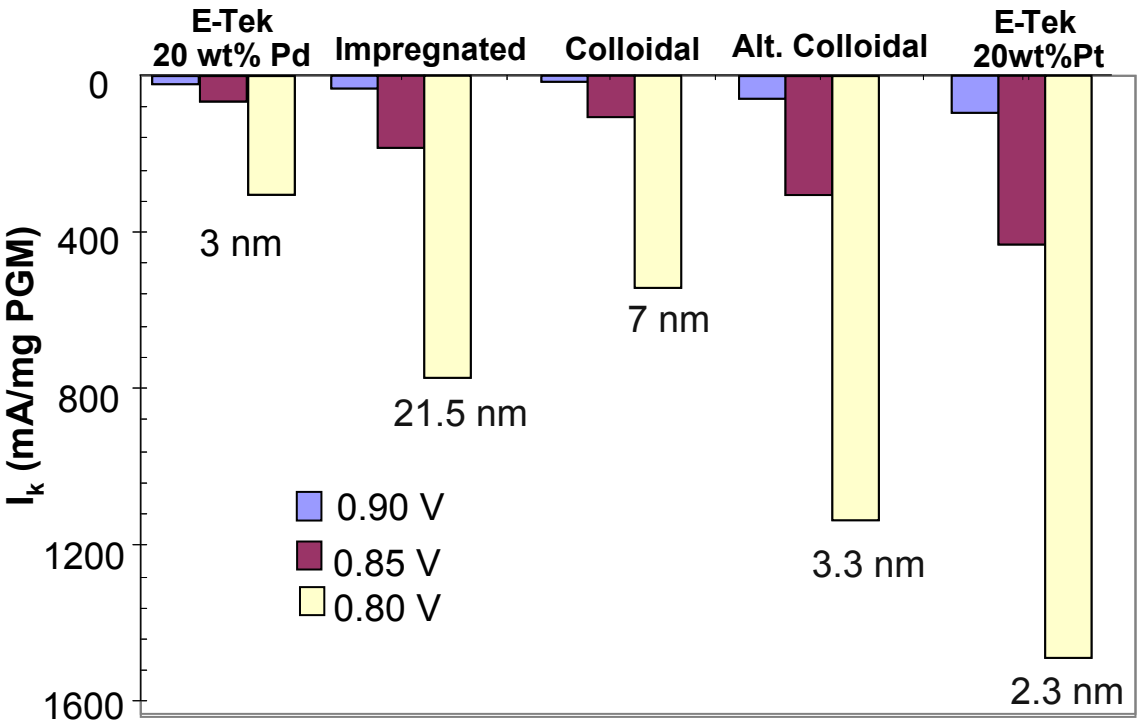


Impregnation
800°C

Colloidal technique provides complete alloying at lower temperatures, resulting in smaller particles, and narrower distribution

Technique, nominal moles Pd: moles Cu	Nano-particle comp.-EDAX, (mol% Cu)	Nano-particle size (nm)
Colloidal, 50:50, 500°C	50.7 ± 5.8	10.0 ± 2.5
Colloidal, 25:75, 500°C	75.2 ± 2.9	7.0 ± 1.0
Impregnated, 25:75, 800°C	67.5 ± 8.9	55.0 ± 14.5
Impregnated, 25:75, 600°C	47.5 ± 10.7	23.3 ± 8.3

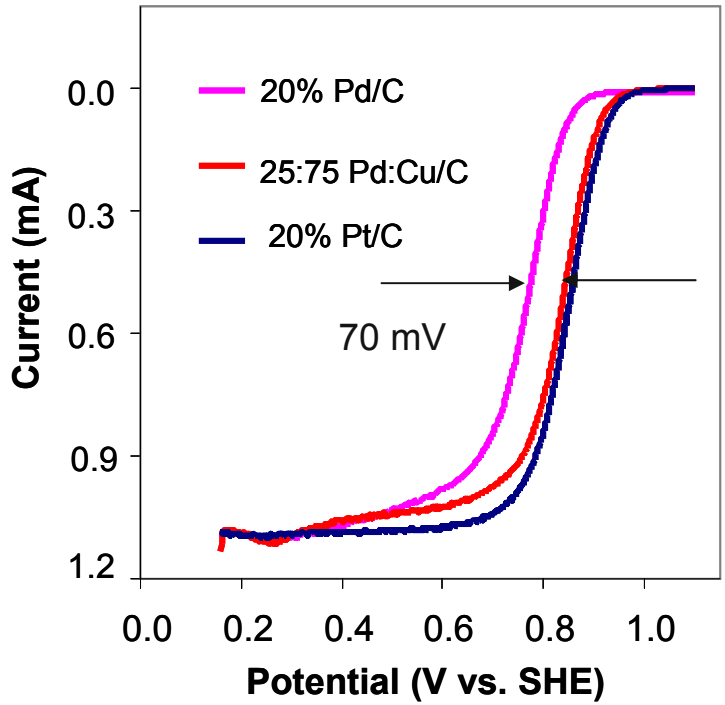
ORR activity summary for Pd-Cu catalyst prepared by different methods



- Activity enhanced ~4x by addition of Cu to Pd
- Activity of ~75% of Pt/C achieved (@ 0.8 V)

Catalyst	$E_{1/2}$ (V)
Pd/C (20wt%, E - Tek)	0.768
Alt. Coll. Pd:Cu/C (25:75)	**0.838**
Pt/C (20wt%, E - Tek)	0.849

RDE, 0.1 M $HClO_4$, 12.5 μg PGM/cm² (Pt and Pd:Cu), 28.6 μg Pd/cm² (Pd), GC area: 0.196 cm², 1600 rpm, RT

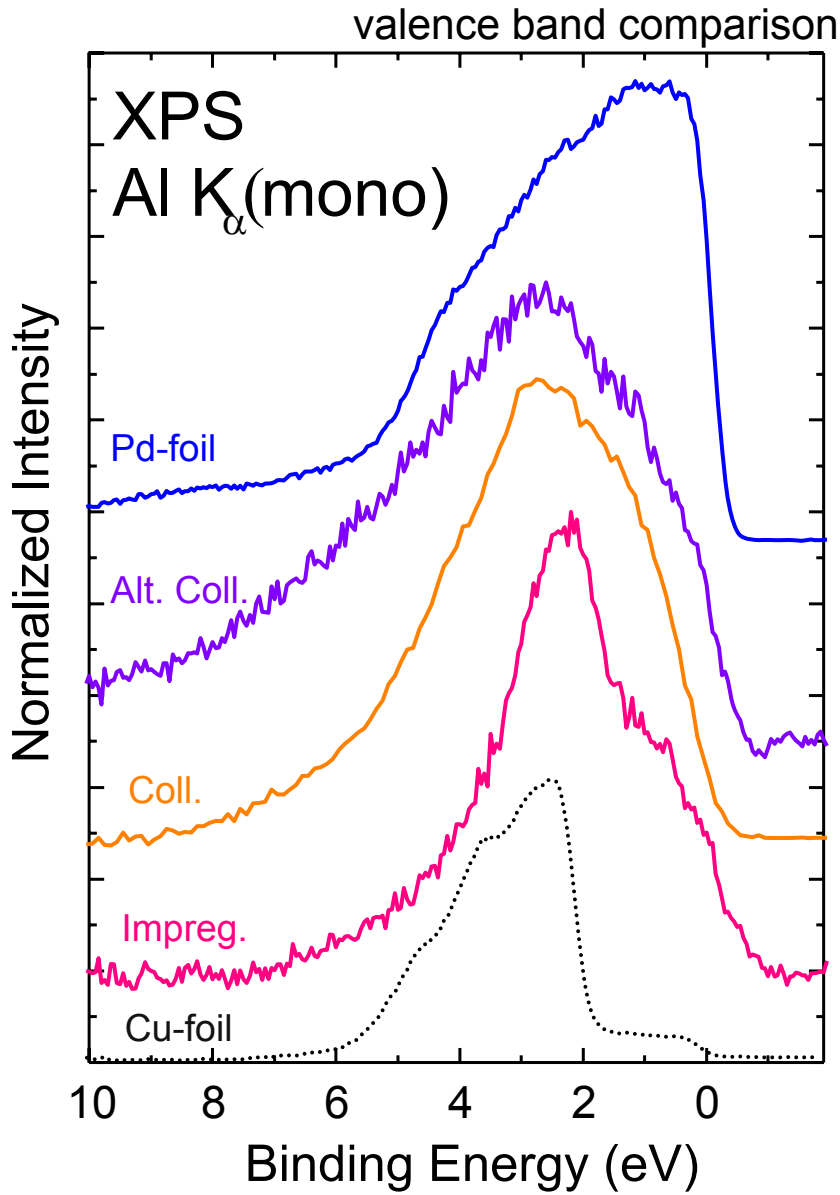


Cu modifies the valence band structure of Pd

- Pd-Cu nanoparticles have strongly modified valence band (VB) structure compared to Pd and Cu
- Nano-particle preparation method effects VB structure
- The spectra are dominated by Pd DOS contributions close to the Fermi energy
- High Pd contribution to VB structure may be indicative of a Pd-rich surface

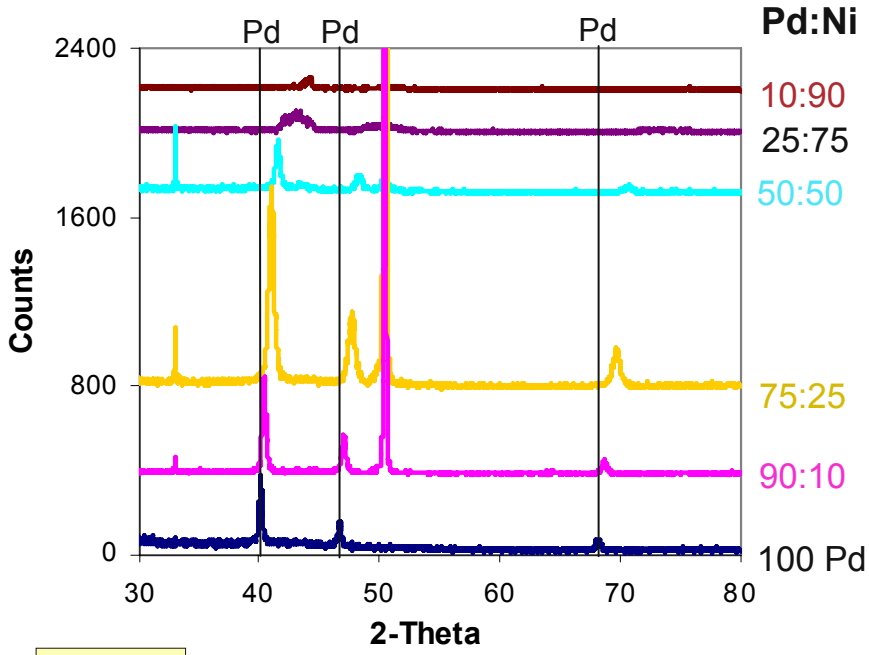
d-band center (occupied states):

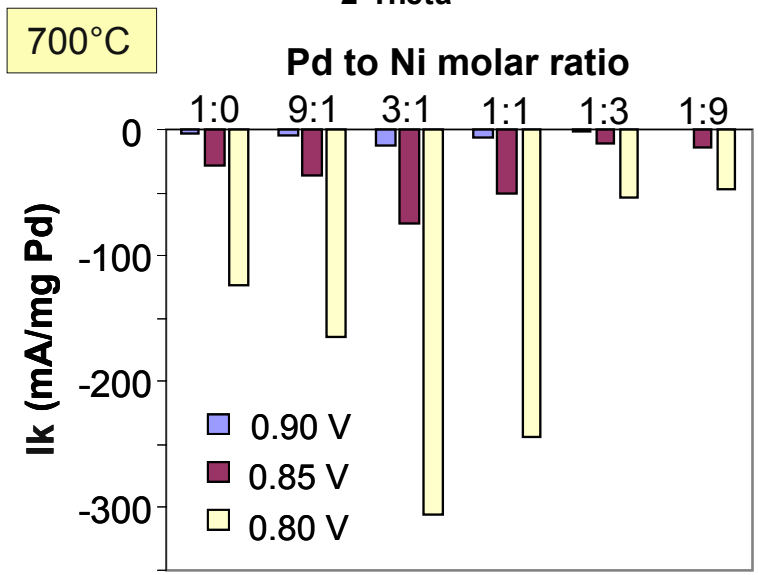
Impreg. PdCu 1:3	2.3 eV
Colloidal Pd:Cu 1:3	2.9 eV
Alt. Coll. PdCu 1:3	**3.7 eV**
Pt foil	**3.5 eV**



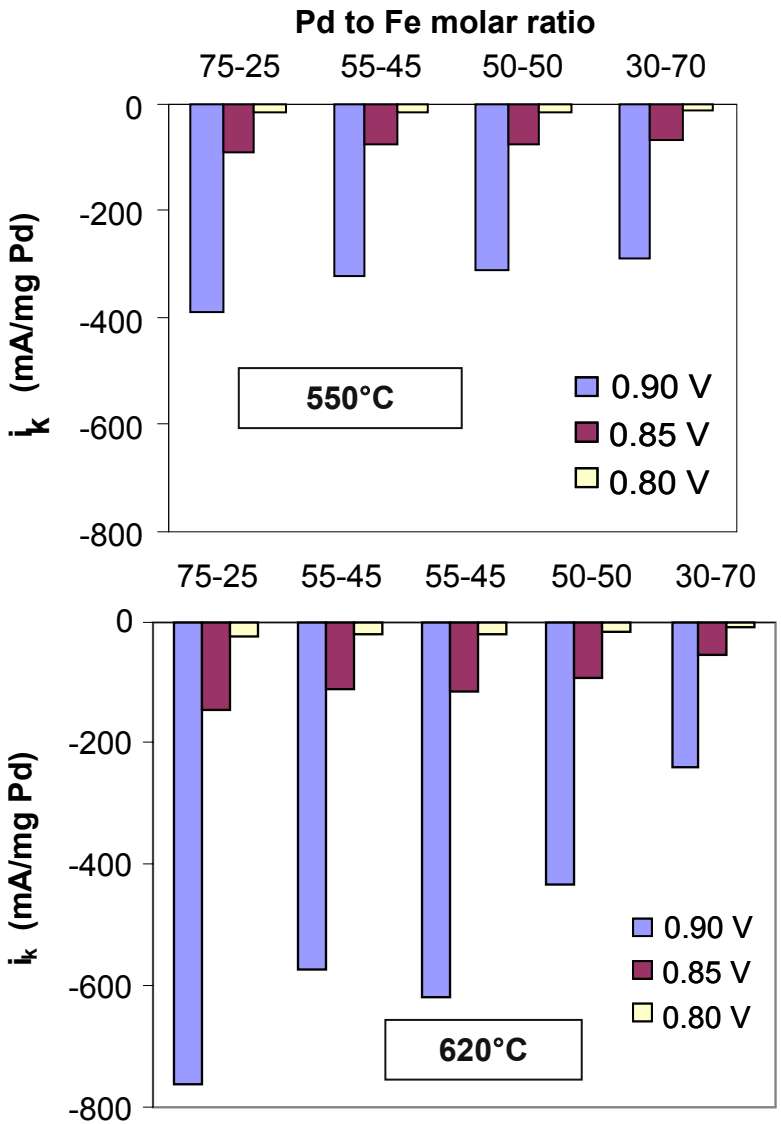
ORR activity of Pd-Ni varied with composition and heat treatment conditions

- Samples prepared by co-impregnation and post-deposition heat treatment
  - *Pd:Ni molar ratios from 90:10 to 10:90*
  - *Temperature: 400 to 700°C*
  - *Atmosphere: 100% H_2 or 3.7% H_2*
- Higher heat treatment temperature enhanced the degree of alloying, but increased particle size
- Higher degree of alloying occurred with a lower level of Ni
- 100% H_2 reduction resulted in lower degree of alloying and lower ORR activity compared to 3.7% H_2
- **Highest ORR activity observed was 50:50 composition, heat-treated at 500°C in dilute hydrogen**



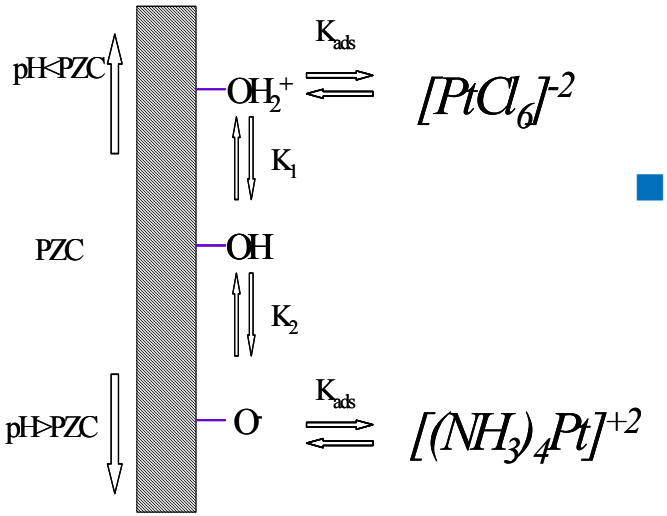


ORR activity of Pd-Fe varied with composition and heat treatment

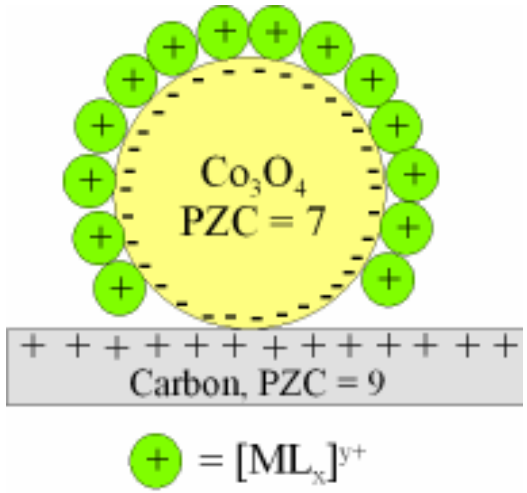


- Samples prepared by co-impregnation and post-deposition heat treatment in reducing atmosphere
  - *Pd:Fe molar ratios from 75:25 to 30:70*
  - *Temperature: 450-620˚C*
  - *Atmosphere: 100% H_2 or 3.7% H_2*
- Low heat treatment temperatures: Lower Pd:Fe ratios yielded the highest ORR activity
- High heat treatment temperatures.: Higher Pd:Fe ratios yielded the highest ORR activity
- **Highest ORR activity observed for 75:25 Pd:Fe heat-treated at 620°C**

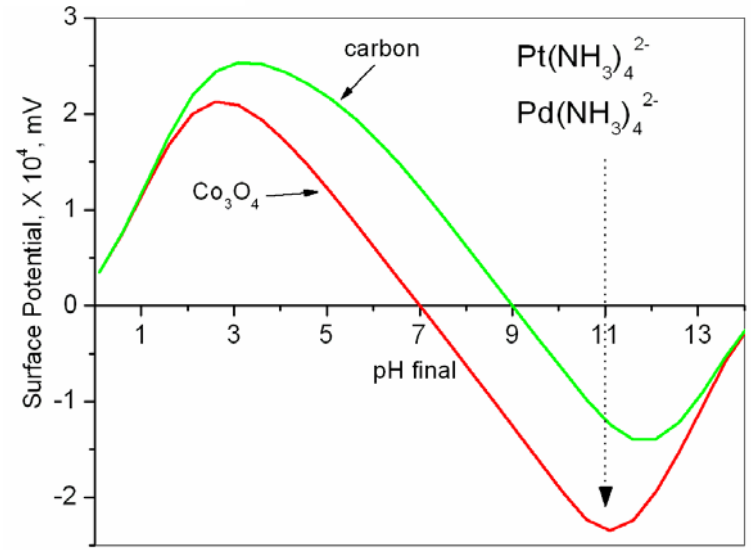
Strong electrostatic adsorption technique for synthesis of core-shell bimetallic nano-particles (UIC)



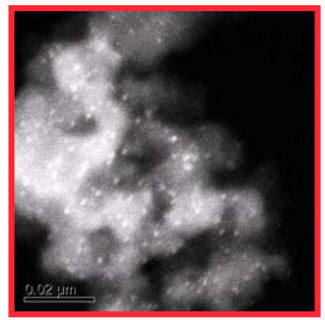
- Impregnate shell metal precursor at a pH between PZCs of support and core metal (or oxide) for selective adsorption



- Determine pH of zero charge (PZC) for carbon support and core metal or oxide
- Adsorb core metal precursor, then either reduce or oxidize



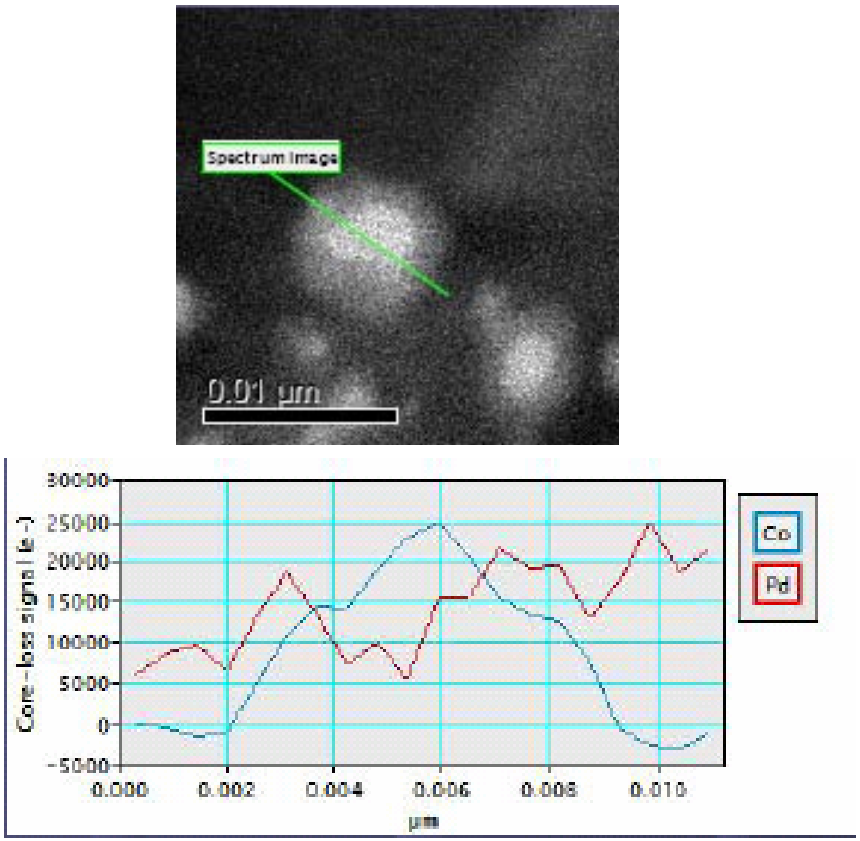
- Reduce in hydrogen to form carbon-supported metal core/shell nano-particles



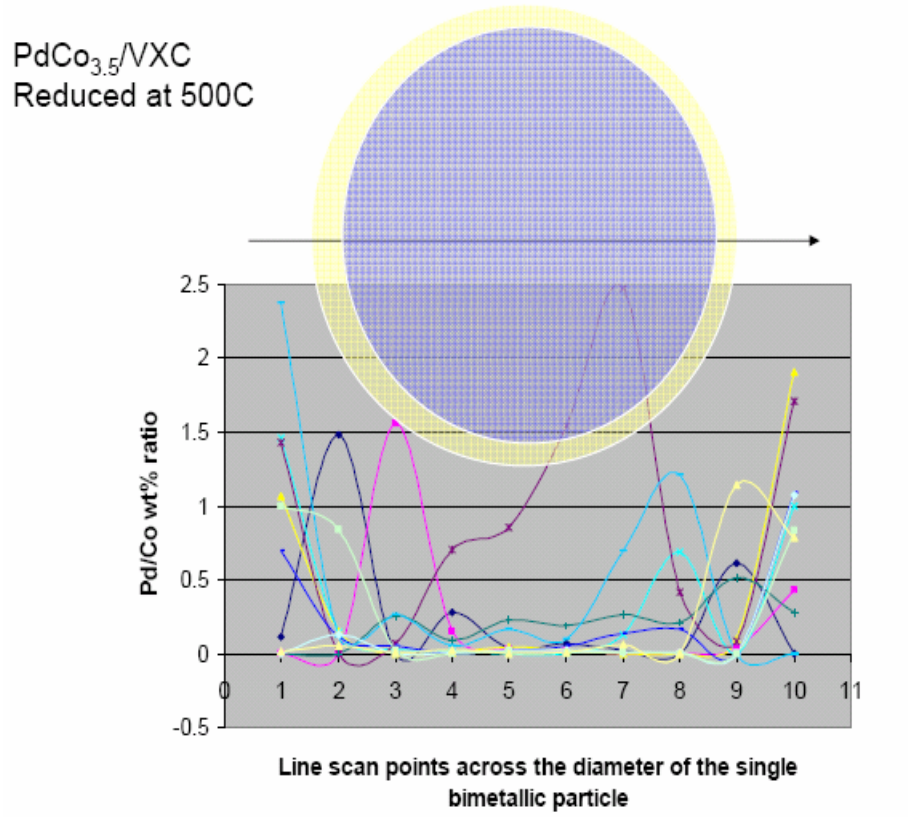
Pd shell-Co core nano-particles have been formed by SEA (UIC)

- A continuous 2 nm thick Pd shell has been formed on a cobalt core (EELS and EDAX)

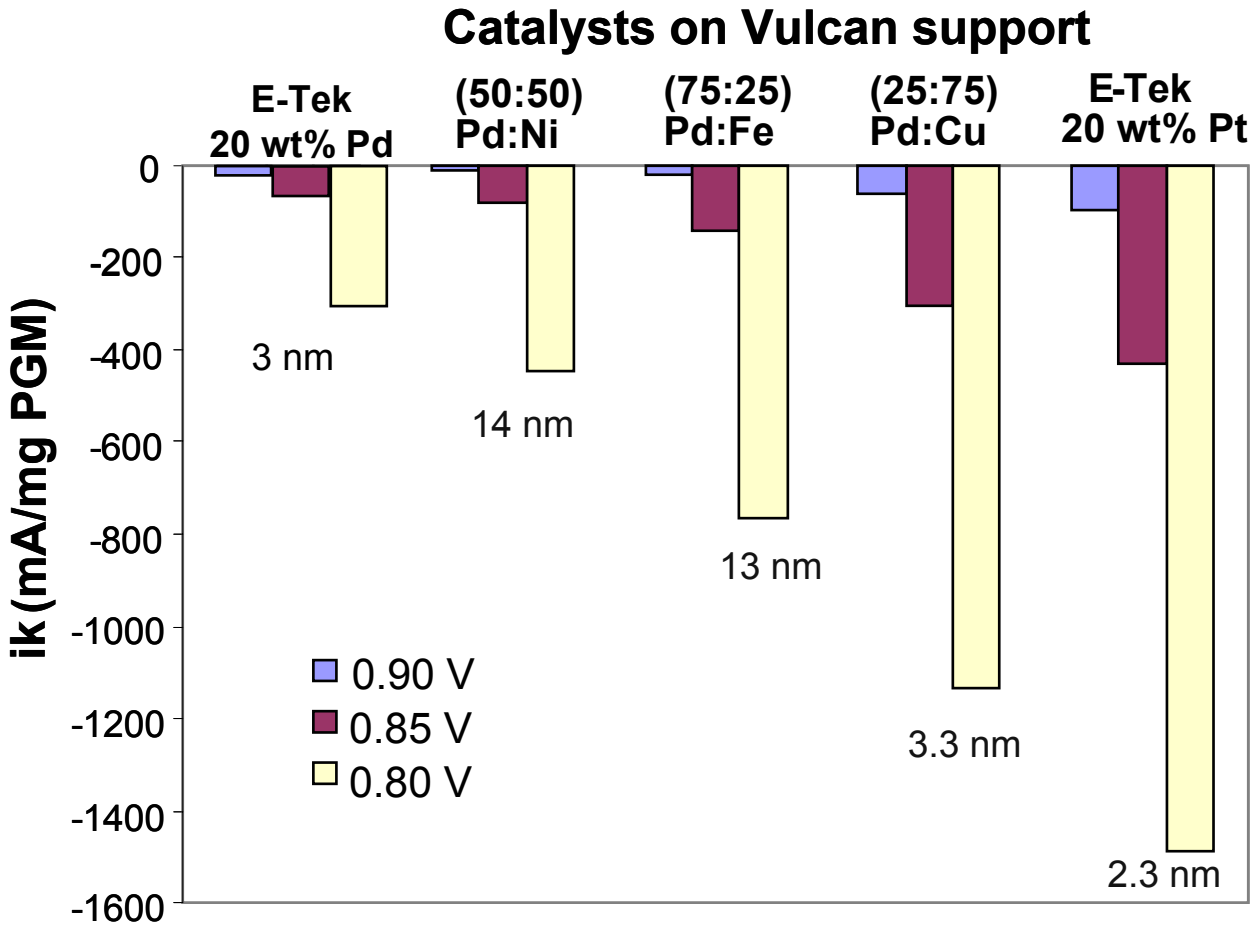
- EELS scan across a particle



- EDAX line scan across a particle



Summary of ORR mass activity of Pd-based catalysts compared to commercial catalysts

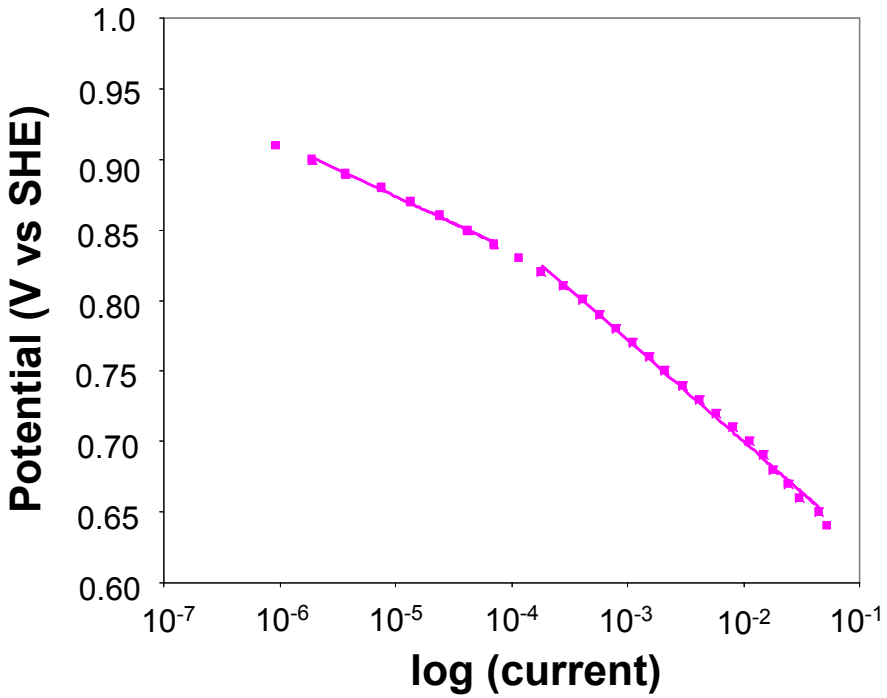


Up to 75% of Pt/C ORR activity achieved with PdCu (~40% the cost of Pt for the same activity)

Kinetic parameters of Pd-based catalysts are similar to Pt's

Vulcan-supported Catalyst	Tafel slope at >0.8 V (mV/dec)	% Conv. to H_2O_2
Pt	63.0	nd
Pd	62.0	<0.05
Pd:Cu 25:75 Impreg.	54.6±0.9	<0.06
Pd:Cu 25:75 Alt. colloid	59.6±3.0	<0.06
Pd:Ni 50:50	60.9±1.3	<0.05
Pd:Fe 75:25	66.3±2.4	<0.07

Number of electrons = 4.1±0.1
(from rotation rate dependence of current)



Milestones/Summary of Progress

- Synthesize and evaluate the oxygen reduction reaction (ORR) activity and stability of nano-particles of with goals of specific activity: 720 μA/cm²; mass activity: 0.44 A/mg PGM (@900 $mV_{iR\text{-}free}$)
  - Milestone (12/07): three palladium alloy systems ✓
  - Milestone (09/08): one palladium alloy system (PdCo) and two rhodium alloy systems (on-going)
- Progress:
  - Highest room temperature ORR specific and mass activity observed:
    - *Estimated **129 μA/cm²** (900 mV)*
      (Acid-treated Pd:Cu 25:75 by impregnation; 21.5 nm)
    - ***0.06 A/mg Pd** (900 mV)*
      (Pd:Cu 25:75 by alternative colloidal; 3.3 nm)
  - Synthesized and characterized a series of Pd-Cu, Pd-Ni, Pd-Fe via co-impregnation; determined the effect of Pd to base metal ratio, post-deposition heat treatment temperature and atmosphere, and acid treatment
  - Developed colloidal technique for Pd-Cu; synthesized and characterized a series of colloidal Pd-Cu catalysts

Summary of progress (cont.)

- Determined that Cu modifies the valence band density of states of Pd
- Developed strong electrostatic adsorption technique for Pd-Co and achieved Co core-Pd shell structure
  - Initial samples exhibited low ORR activity
- Determined effect of Pd particle size (1.2 to 20 nm) on ORR kinetics
  - 5 nm particle size shows highest ORR mass activity
- Fabricated first model system series
  - successive deposition of Pd on Cu at room temperature
- Calculated preferred reaction pathways and barriers for two possible O_2 reduction reaction mechanisms on slabs of pure metals using DFT
  - Dissociative mechanism through –OH formation
  - Associative mechanism through –OOH formation
- Calculated ReaxFF potentials for Pd and PdCu

On-going and future work (FY'08 and FY'09)

- **Computational analyses**
  - Determine energetics, including barriers, for dissociative and associative ORR mechanisms on PdCu slabs
  - Study surface segregation in PdCu alloy slabs (QM) and in nano-particles (ReaxFF)
  - Investigate solvation and coverage effects for the ORR on Pd and PdCu alloys
  - Fit ReaxFF to the cathode chemical reaction energies and perform simulations of cathode reactions on PdCu nano-particles

- **Model systems and nano-particle characterization**
  - Study effect of annealing, determine surface segregation, and measure ORR activity on PdCu model system
  - Prepare and characterize Pd on Ni, Pd on Fe, Cu on Pd, Ni on Pd, and Fe on Pd model systems
  - Perform depth-dependent electronic structure characterization using tunable synchrotron radiation

- **Nano-particle fabrication, activity and stability characterization**
  - Prepare significant quantities of most active PdCu catalyst for MEA testing
  - Deposit Pd shell on PdCu alloys prepared by colloidal technique
  - Develop colloidal technique for PdNi, PdFe, and PdCo alloys and SEA technique for PdNi, PdFe, and PdCu
  - Determine stability of all Pd alloys to potential cycling
  - Characterize Rh-based alloys fabricated by co-impregnation